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A SEMICONDUCTOR MATERIAL RESEARCH PROGRAM

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Teledyne Isotopes
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Peter Alexander and Herman Shulman

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SUMMARY

An experimental study has been performed to ascertain the suitability of using germanium-silicon alloy single crystals to fabricate charged particle detectors. It is hypothesized that by selecting a suitable Ge/Si ratio - and thus defining the band gap value - operation of the detector at selected temperatures between +20°C and -195°C should be possible. The mixed constituent nature of the alloy lattice should also endow the alloy detectors with radiation damage resistant properties. This study has revealed that charged particle detectors can be fabricated from germanium-silicon alloy crystals. These detectors are operable at temperatures above -75°C. Preliminary results indicate that the alloy may possess radiation damage properties superior to either germanium or silicon.

INTRODUCTION

The superior energy resolution provided by semiconductor nuclear radiation detectors has made widespread their use in charged particle experiments. Commercially available semiconductor detectors sensitive to charged particles are normally fabricated from either silicon or germanium. These detectors may be fabricated in a number of different configurations. Among

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these are surface barrier, diffused junction and lithium ion drift (p-i-n) configurations. Although silicon detectors may be operated at 20°C with reasonable resolution, it is necessary to employ operating temperatures of < -75°C for optimal energy resolution. Due to the smaller band gap of germanium, detectors made from this material yield superior energy resolution but must be maintained at a temperature of -195°C in order to function satisfactorily. Various surface passivation techniques have been perfected for silicon detectors so that they may be demounted and stored on a shelf when not in use. To date no equivalent technique is available for use on germanium detectors, thus they must be constantly maintained in vacuum. Germanium detectors also must be continuously maintained at low temperature in order to prevent precipitation of the lithium which has been drifted into the detector to compensate the germanium impurities. Loss of this lithium renders the detector inoperative. Lithium precipitation proceeds at a very low rate in silicon at 20°C, thus this type of detector may be maintained at room temperature without deleterious effects.

Germanium has a higher stopping power for charged particles than does silicon. This property, attributable to the higher density and atomic number of germanium, renders it a more desirable material than silicon from which to fabricate a detector for high energy charged particle spectroscopy. The range of a 43 MeV proton in silicon is 1 cm while it is only 0.7 cm in germanium.

Both germanium and silicon detectors suffer radiation damage with sufficiently large radiation dosages. The problem of radiation damage is serious since its effects limit the usable life-time of solid-state detector devices. Detectors operating in orbiting space vehicles where the radiation levels may be many orders of magnitude higher than those encountered at ground level, will be most adversely affected.

The major effect of radiation damage on solid state detectors is a reduction in the number of available charge carriers collected. Radiation damage to solid state detectors induced by photons, electrons and protons results primarily from displacements within the crystal littice. Atoms are displaced either through direct collision with the primary radiation or by interaction with secondary products produced in the primary interaction. Displaced lattice components result in interstitial-vacancy pairs which can migrate within the crystal and interact with each other and with various crystalline impurities and imperfections. Heavy charged particles and fast neutrons produce regions of high displacement density forming a localized space charge zone which is depleted of electrons. Such zones serve to restrict current flow in the semiconductor detector. The magnitude of the above effects is a function of both the temperature and the orientation of the semiconducting crystal.

The ideal solid-state detector for space applications would combine the desirable properties of a germanium detector (high resolution, stopping power, large depletion depths available in p-i-n configuration) with the operating temperature range of a silicon detector. In principle, this can be achieved by a judicious alloying of germanium and silicon.

The germanium-silicon alloy detector might possess an additional property not present individually in either silicon or germanium. It is likely that the mobility of the primary radiation defects, interstitial atoms and vacancies, will be retarded in the multi-element lattice. Interstitial motion in such a lattice would be sterically hindered. Similarly, the migration of vacancies on their own sublattice will also be hampered.

In pure silicon as in pure germanium both interstitials and vacancies are sufficiently mobile to interact with dopants and other defects so as to produce stable secondary complexes. Removal of these radiation induced complexes by annealing requires a temperature so high as to destroy the properties of the germanium and silicon which enable it to function as a detector. In the germanium-silicon alloy, the formation of complexes will be hindered not only by the low vacancy-interstitial mobility but also by the thermal annealing which may be expected to proceed at reduced temperature. If the detector bias is maintained during the annealing cycle, the resulting lithium ion drift will tend to compensate both primary and secondary damage effects. Such an "in situ" cycling procedure should enable greatly extended detector operating lifetimes.

This research program is concerned with an investigation of the physical properties of germanium-silicon alloy crystals and radiation detectors fabricated from them. The various phases involved in this investigation are listed below.

a) Procurement of germanium-silicon alloy single crystals of various Ge/Si ratios.

b) Investigation of physical properties of the alloy crystals.

c) Fabrication of p-i-n detectors.

d) Study of detector properties.

e) Radiation damage studies.

Details of these investigations are presented in the following sections.

2. GERMANIUM-SILICON ALLOY SINGLE CRYSTALS

The specifications for germanium-silicon alloy crystals used for nuclear radiation detector fabrication are consistent with the crystal requirements necessary to produce good germanium or silicon detectors. The physical properties desired in a detector grade germanium-silicon alloy crystal are listed below:

a. The alloy should be single crystal 1-1-1 orientation with no twinning or gross lineage.

b. Dislocation density less than 10,000/cm^2.

c. Resistivity 20 - 500 ohm-cm, gallium or boron doped.

d. P-type conductivity achieved without compensation doping of n-type material.

e. Centerless ground crystals are to have a diameter of 1.5 cm and a length of > 5 cm.

f. Metals and carbon content less than 1 ppm. Oxygen content < 10^{15} atoms/cm^3. Low oxygen content to be obtained by use of a clean crucible and an atmosphere of helium or argon (80%) and hydrogen (20%). Gases must be of spectroscopic purity grade and passed through a gas dryer-filter.

g. Variation in crystal resistivity profile along face from crystal center to outer edge must be < 10%. The homogeneity of the crystal must not vary by more than 1% per cm of crystal length.

h. Charge carrier lifetime at 20°C must be > 10 μs.

The germanium-silicon alloy single crystals are generally Czochrolski pulled although it is also possible to grow the crystals in a horizontal boat. Contamination of the high purity germanium and silicon by impurities in either the boat, the crucible containing the melt, or the atmosphere in the pulling apparatus is always a problem. The major difficulty in pulling large single crystals of the alloy arises from the segregation of the germanium and silicon. Generally the crystals are pulled using an alloy seed of appropriate composition. In order to pull a germanium-silicon alloy crystal containing 10% germanium - 90% silicon, the heated melt might initially contain 30% germanium - 70% silicon. A 5% germanium - 95% silicon seed would be used at extremely slow pull and

rotation rates, typically 2mm/hour and 10 rpm respectively. At such low rotation rates the heavier germanium tends to segregate. As the 10% germanium crystal is pulled, the germanium-to-silicon ratio in the melt changes, requiring continual readjustment of the melt temperature. These are some of the problems which make it difficult to produce large nuclear radiation detector grade germanium-silicon alloy single crystals. The literature[1] contains references to germanium-silicon alloy crystals grown in the ranges 0 to 23 weight % germanium in silicon and 0% to 13% silicon in germanium. Generally these crystals were not of a size and purity level necessary for semiconductor detector fabrication. A crystal containing 7% germanium was obtained from the same lot as those in reference 1 and was found to be unsatisfactory for detector production.

A large number of potential suppliers were contacted in order to procure germanium-silicon alloy crystals meeting the specifications outlined earlier. A list of these contacts will be found in Appendix A. Two germanium-silicon alloy crystals containing 11.0% germanium by weight were procured from the Elmat Corp. Only one of these crystals could be used since the other showed evidence of twinning. Three crystals ranging in germanium content from 10.5% to 12.3% by weight were received more recently from Metallurgie Hoboken. Characteristics of these four usable single crystals are presented in Table 1.

TABLE 1

SOME PROPERTIES OF SELECTED GERMANIUM-SILICON ALLOY CRYSTALS USED TO FABRICATE DETECTORS

Crystal No.	6599-1	00121	00122	00123
Resistivity	100-300Ωcm	23-30Ωcm	200-400Ωcm	155-245Ωcm
Etch Pit Density	< 10,000	< 100	< 6000	< 100
Weight	25 g	51 g	57 g	167 g
Length	50 mm	65 mm	44 mm	79 mm
Diameter	10 to 20 mm	20 mm	24.5 mm	28 to 39 mm
Ge Content by Weight	11.0%	12.1%	10.5%	12.3%
Type	p	p	p	p
Orientation	1:1:1	1:1:1	1:1:1	1:1:1
Physical Perfection	Excellent	Excellent	Excellent	Excellent
Dopant	B	B and Ga	B and Ga	B and Ga

The germanium-silicon alloy measurements described in the following section were performed on slices from the above crystals. A large number of additional germanium-silicon alloy crystals of lesser quality were received from other vendors. A list of these crystals and how they fared as detectors will be found in Appendix B.

3. PHYSICAL PROPERTIES OF THE GERMANIUM-SILICON ALLOY CRYSTALS

After the germanium-silicon alloy crystals were received they were examined to see that they conformed to the specifications laid out in the preceding section. This involved determining such properties as: the size of the crystal, the dislocation density, the degree of crystal perfection, the germanium content of the crystal and the oxygen impurity concentration of the alloy crystal. As soon as

they were received the germanium-silicon alloy crystals were measured and weighed. Next they were waxed onto a ceramic block and appropriately sliced with a diamond wheel. The longitudinal resistivity profile of the ingot and radial resistivity profiles of the slices were measured with a four-point probe and ASTM F43-64T techniques[2]. A preferential etch was performed on selected slices taken from the various alloy ingots in order to examine crystal dislocation densities. To perform the preferential etch, a 0.25 cm thick crystal was cut, lapped with 500μ silicon carbide and aluminum oxide, then cleaned ultrasonically using tricholorethylene, and washed successively in alcohol and distilled water. The wafer was placed in a mixture of 2:1 nitric acid, hydrofluoric acid at 0°C and etched for 45 seconds. Next the wafer was quenched with distilled water and then immersed in a mixture of acetic acid, nitric acid and hydrofluoric acid (10:3:1) for four hours. After quenching with distilled water the wafer was removed and examined. None of the specimens exhibited high dislocation densities at the center; however, some samples contained outer rings with high dislocation densities. These outer rings were removed before any further processing. The etch pit densities of a few specimens were determined and in all cases found to agree with the manufacturers' values.

All specimens were examined for twinning, gross lineage, and slip. These phenomena reflect the degree of crystal disorder. A high degree of crystal perfection is required in order to produce a semiconductor detector with superior energy resolution.

A twinned crystal is one in which the lattice is of two parts related to each other in orientation as mirror images across a coherent planar interface.

In this case the interface is the (1-1-1) plane. A twin boundary appears as a straight line at the intersection of a (1-1-1) plane and the etched surface. Two parallel twin boundaries separated by a few crystal lattice planes form a twin lamella which appears as a straight grooved line. With the exception of one Elmat crystal no twinning was observed in the specimens examined.

Gross lineage is a low angle grain boundary resulting from an array of dislocations. None of the specimens examined exhibited gross lineage in the center of the crystal although some specimens showed lineage near the high dislocation density outer ring. This area was then removed.

Slip indicates a movement of one part of the crystal with respect to the rest. Slip as evidenced on a (1-1-1) surface appears to the unaided eye as a triangle or a six-pointed star. Under a microscope slip appears as a line of dislocation etch pits in which all the triangular etch pits point in the same direction. This line of etch pits will lie in a (1-1-0) direction. All of the specimens examined showed signs of etch pits that covered the entire cross section. This resulted in a clearly visible triangle or six-pointed star. However, this slip was not sufficiently severe to cause problems in detector fabrication.

The germanium content of all crystals was initially determined by a density measurement. For crystals of a regular shape the dimensions and weight sufficed to yield the density. The volume of crystals of an irregular shape was determined by a water displacement method. The average germanium content of both the entire crystal and selected slices taken perpendicular to its axis were then determined from the known density variation of germanium-silicon with germanium concentration[3]. The germanium content determined by the method described above was cross checked in a number of cases using chemical and x-ray diffraction techniques.

Using the chemical technique, a slice from the alloy is fused with sodium peroxide and leached in hydrochloric acid. Then germanium tetracholoride is distilled from potassium permanganate and trapped in sulfuric acid. Germanium disulfide is precipitated from the sulfuric acid using hydrogen sulfide. Following dissolution and reprecipitation, the germanium disulfide is ignited to germanium dioxide for weighing.

The germanium-silicon alloy slices are prepared for x-ray diffraction measurement of the lattice parameter by grinding the crystal to be examined to 100 mesh powder. An x-ray generator was used to irradiate a copper target. The resulting Cu K_{α_2} and K_{α_1} diffraction peaks were scanned with a wide range diffractometer using a pure silicon standard for reference. The germanium concentration of the sample was calculated using the lattice parameter determined from the x-ray peak locations. Typical germanium weight content as measured for alloy crystal 00122 (see Appendix B) is 10.5±0.3% by density measurement, 10.8±0.3% by chemical analysis, and 10.47±0.08% by lattice parameter measurement. The germanium content of slices from this crystal taken perpendicular to the axis at various points along its length was found to vary by less than 10%.

The presence of oxygen is known to preclude the fabrication of good semiconductor detectors, usually by inhibiting lithium drift. The oxygen content of several ingots evidencing low drift rate and poor detector performance, was examined in order to try to determine if oxygen contamination was the reason for this behavior. Infrared absorption techniques at approximately 9 microns were used for these determinations. No oxygen contamination could be discerned using this technique as the oxygen sensitivity limit of 5×10^{16} atoms/cm^3 using this method is well above the threshold value of 10^{14} to 10^{15} which is necessary to perturb detector drift conditions. An alternative method was employed in an effort to measure oxygen contamination levels with greater sensitivity. This method involves diffusing lithium homogeneously through a slice of alloy at

~600°C, quenching the material, then following the time rate of change of the room temperature Hall Coefficient as lithium precipitates out of solution. This technique has been successfully applied[4] to the measurement of oxygen concentrations on the order of 10^{14} atoms/cm^3 in pure germanium crystals. No change in free carrier concentration of the germanium-silicon alloy was observed in these experiments indicating that the excess lithium was not precipitating at the measurement temperature of 20°C. The same measurements were carried out at 100°C but again no change in free carrier concentration was observed. This indicates that this method for measuring low level oxygen concentrations in germanium as described above did not function to yield low level oxygen concentration values for the alloy.

In order to make good semiconductor diodes it is necessary to diffuse lithium into the material to just the proper depth. If lithium is diffused too deeply, a thick "dead layer" results on the face of the detector. If lithium is not diffused deeply enough, oxidation and surface preparation will remove the lithium before it can be drifted into the material. Although the germanium-silicon alloy under study is 90% silicon by weight, it is not at all obvious that the diffusion rate of the alloy will be the same as that for silicon. It was, therefore, necessary to study the diffusion of lithium in the germanium-silicon alloy as a function of temperature and Ge/Si ratio.

An investigation has been made to determine the value for the ratio of the diffusion constants, $D_{alloy}/D_{silicon}$ at various temperatures between 250°C and 650°C. Lithiated slices of both silicon and germanium-silicon alloy were heated to a preselected temperature. The slices were removed from the oven and 10μ thickness were successively lapped from each slice. After each lapping, the resistivity of the lapped face was measured with a four-point probe. From the successive resistivity measurements on each sample a lithium

diffusion profile could be constructed giving the lithium concentration as a function of depth perpendicular to the crystal face. Such a curve is presented in Figure 1. These diffusion curves were generated for specimens of germanium-silicon alloy (10% germanium by weight) and pure silicon at temperatures of 250, 350, 450, 550, and 650°C. At several of these temperatures a number of pairs of slices were diffused for different time intervals to make sure that the mechanism being measured was exclusively a diffusion effect. It was found that the diffusion constant ratio remains at approximately 0.9 over this range of temperatures.

The rate at which lithium can be drifted into germanium-silicon alloy under the influence of an applied electric field was studied as a function of temperature in the range of 100°C to 160°C. The lithium drift rate is an important quantity in that it reveals how deeply a germanium-silicon alloy slice may be lithium compensated in a given time period. Anomalous behavior in the drift-depth versus time function can also reveal the presence of various impurities in the crystals. The drift depth measurements were performed by first vacuum evaporating lithium onto the face of a germanium-silicon alloy slice. Next the alloy slice was transferred to an argon atmosphere furnace in which it was heated at 400°C for 10 minutes giving a lithium diffusion depth of ~200μ. After diffusion the slice was etched and placed on drift in a silicone fluid medium maintained at the desired temperature. The progress of the n-i and i-p junctions were monitored by the copper stain technique. The junction position as determined by the copper stain method was verified by measuring the resistivity profile of one drifted alloy slice using the four-point probe and successive lapping technique described previously. The best drift temperature for these alloy samples as determined from these measurements appears to be ~150°C.

The change in depth of the intrinsic region was followed at a given temperature for about 12 days with a fixed applied reverse bias of 75v. At drift temperatures below 100°C very little drifting takes place. At temperatures above 160°C diode thermal runaway is encountered. The intrinsic depth versus drift time curve is plotted in Figure 2 for temperatures of 120°C and 150°C. Comparison drift curves for germanium and silicon are also presented in Figure 2. It may be observed that germanium-silicon alloy drifts considerably more slowly than either germanium or silicon.

In order to register, or count, a photoelectric interaction in a germanium-silicon alloy detector, the lifetime of the injected electron-hole pairs must be sufficiently long to permit their collection at the surfaces where electrical contact is made. The time necessary for this process is a function of the mobilities of the charge carriers, the physical dimensions of the detector and the magnitude of the applied electric field. Typical charge collection times are of the order of 20 ns. If the carrier lifetime is not sufficiently long to permit collection of all injected carriers, the relative statistical error associated with the collection process will be increased and the detector resolution will be correspondingly degraded. The injected carrier lifetime is also important in another respect. Anomalous time behavior of the excess carrier concentration usually indicates the presence of trapping or impurity sites in the crystal. The observed carrier lifetime will be altered in a way which is dependent on whether the trapping sites have long or short trapping time constants.

The lifetime of carriers in germanium-silicon alloy samples was determined by measuring the decay of the photoconductivity signal due to injection of carriers induced by a pulsed xenon flash-tube. In an unlithiated sample at 20°C the lifetime was found to be ~40 μs. At 137°K this value increased to ~20 ms

indicating the presence of considerable trapping. In a sample into which $\sim 10^{15}$ lithium atoms/cm^3 were diffused, the lifetime at 137°K was reduced to 4 μs. The measurements suggest that the unlithiated germanium-silicon alloy contains a substantial number of trapping sites which empty slowly at low temperature. When the sample is lithiated these traps are well compensated and the lifetime is determined primarily by recombination at the excess lithium sites.

4. DETECTOR FABRICATION AND TESTING

The fabrication techniques employed for germanium-silicon alloy detectors are substantially the same as those used for silicon and germanium detectors. These techniques have been recounted in detail in the literature[5,6]. The procedure employed is given briefly below.

A. Preparation of the Crystal

1. A wafer 2 to 4 mm thick is cut from an ingot of germanium-silicon alloy which has previously been subjected to general physical inspection. The cut is made with great care using a liquid cooled diamond saw.
2. The wafer is lapped on both faces with 500μ silicon carbide and then with aluminum oxide. Next the wafer is cleaned with distilled water and alcohol.
3. The edge and one face of the wafer are masked with tape and lithium is evaporated onto the unmasked face at a pressure of $< 10^{-6}$ mm of mercury.
4. The wafer is rapidly transferred to a furnace held at ~400°C and containing an argon atmosphere. Lithium is diffused into the wafer for ~10 minutes.

5. After removal from the oven the edges of the wafer are cleaned and both faces are masked with a tape which is impervious to acid. Next the wafer is etched for 2 minutes in CP-4, rinsed in distilled water and blown dry with pressurized nitrogen. The tape is then removed.

6. The resistivities of the n and p faces are checked with a 4 point probe and the forward and reverse bias resistance of the wafer are determined. The n face resistivity must be $< 0.02\Omega$ cm, the p face resistivity should agree with that of the ingot from which the wafer was cut, and the ratio of foward to reverse bias resistance should be < 0.1. Unless these criteria are met steps 2 through 6 are repeated.

B. Lithium Drift

1. The wafer is placed in a nonane bath maintained at a temperature of ~100°C in the configuration shown in Figure 3. A reverse bias of ~150 volts is applied. The resulting current should be < 25 ma or steps 2 to 7 are repeated. Internal heating (4 watts) raises the temperature at which the drifting takes place above the initial temperature of the nonane fluid.

2. The depth to which lithium has compensated the alloy is monitored periodically using the copper staining technique. By reverse biasing the diode while staining, the n-i and p-i junctions are made visible. The technique correlates reasonably well with the capacitance method for measuring drift depth, where

$$\text{Drift depth (cm)} = 1.2 \times \frac{\text{Diode Area (cm}^2\text{)}}{\text{Capacitance (pf)}}$$

In a good detector the capacitance is not a strong function of the applied reverse bias voltage.

C. Level Drift

1. When a detector has reached the desired depth it is removed from the drifting bath and given a level drift. This consists of placing the detector in a nonane bath a ~20°C and drifting it for 24 hours at high voltage and low current. This drift provides a more uniform lithium compensation.

D. Testing Gamma Ray Response

1. The detector is mounted in a test dewar and checked for reverse bias leakage current at room temperature and at liquid nitrogen temperature. The leakage current at room temperature must be less than 10 μa at 1000 volts/cm of detector depth or else the detector is boiled in alcohol. If this does not produce the desired performance the detector edges are etched in hydrofluoric acid and rinsed with alcohol and distilled water. If this fails the edges are lapped with aluminum oxide and the detector re-etched in CP-4.
2. A ^{133}Ba gamma ray source is placed against the outer face of the cooled test dewar containing the alloy detector and the detector gamma ray spectrum is observed. The electronic system used for this operation is shown schematically in Figure 4. The high voltage and amplifier time constants are adjusted to obtain optimum gamma ray resolution.
3. If the detector performance is satisfactory the following measurements are performed:

   (i) Capacitance versus applied bias

   (ii) Reverse bias versus current at -195°C, -75°C and +20°C

(iii) Gamma ray resolution at 81 keV and 356 keV

4. Next the detector is either used in the radiation damage experiments, stored to test long term stability at room temperature, or a thin gold window is fabricated on the p-face as described below.

E. Application of a Thin Gold Entrance Window

1. After the detector is removed from the test dewar a section of the p-face is removed by masking the outer portion and etching the center with CP-4. The determination of when the p-layer is removed and the i-layer is reached is performed using a four-point probe and the copper stain technique. The detector is carefully cleaned with distilled water, alcohol, and distilled water. Mylar tape is used to cover the n-face and the detector is etched for 1 minute in CP-4. The CP-4 is constantly diluted with distilled water until all traces of acid are removed. The detector is now mounted on a mask and gold is evaporated onto the i-face at a pressure of 10^{-6} mm.
2. The detector is then mounted in the test dewar. An ^{241}Am source emitting 5.5 MeV alpha particles is mounted inside the dewar. The alpha particle resolution, and reverse bias leakage current curves are determined at -195°C, -75°C and +20°C.

5. DETECTOR PROPERTIES

High quality photon detectors were fabricated from crystals number 6599-1, 00121, and 00123 (see Section 3). A typical set of reverse bias current characteristics for one of these detectors may be found in Figure 5. These characteristics were measured at -195°C, -75°C and +20°C. The alloy detectors yielded good gamma ray resolution at temperatures up to -75°C. At room temper-

ature the resolution was greatly degraded due to surface leakage. A grooved or guard ring detector configuration may substantially improve this response[6]. For temperatures between -75°C and -195°C typical resolution for gamma rays was 4 keV. This value of 4 keV can be completely attributed to preamplifier noise as the capacitance of the alloy diodes was roughly 80 pf. The gamma ray response of the diodes was used as an indicator to determine whether the detector properties were sufficiently good to justify fabrication of a thin gold entrance window on the detector for charged particle measurements. A thin gold entrance window must be applied to the alloy detector in order that alpha particles, electrons, and protons will not be too highly attenuated in the 100μ thick n-type dead layer on the front face of the alloy detector. This layer of gold has a thickness of approximately 30 $\mu g/cm^2$. It is evaporated onto the i-region as described in the preceding section. Even this very thin (10 to 30 $\mu g/cm^2$) gold window scatters and degrades the energy of the incident charged particles sufficiently that the detector resolution is limited to 10 - 20 keV for the ^{241}Am alphas whose energy averages ~5.5 MeV. Thin gold entrance windows were fabricated on a number of germanium-silicon alloy detectors. In some case the window was not successfully applied on the first several tries. At this point the germanium-silicon wafer was generally so thin, due to the repeated lapping and etching, that it fractured. Both the reverse bias leakage current at various temperatures and the alpha particle resolution were measured on detectors to which gold windows had successfully been attached.

The performance characteristics of the gold window germanium-silicon alloy detectors fabricated under this program are presented in Table 2. The Table also includes entries corresponding to diodes made from low germanium content material received early in the program. An ^{241}Am alpha spectrum as recorded by one of these detectors is presented in Figure 6. All detectors

made from Hoboken material operated with substantially the same resolution at -75°C as they had at -195°C. Detectors made from other alloy ingots generally exhibited a fwhm at -75°C which was double the value at -195°C.

TABLE 2

PROPERTIES OF GERMANIUM-SILICON ALLOY DETECTORS WITH THIN GOLD ENTRANCE WINDOWS

Alloy Ingot from which detector was fabricated (see Appendix B)	Weight % Ge	Detector Number	Reverse Bias Current at 100 volts			^{241}Am Alpha Resolution (fwhm)	
			-195°C	-75°C	+25°C	at -195°C	at -75°C
39	0.81	GD-39-4	.07 na	- na	2.2μa	60 keV	65 keV
85	1.6	GD-85-3	0.1	7	4.0	33	82
M-1	1.1	M-1-1	1.0	-	20	43	76
M-1		M-1-3	1.6	-	17	~115	-
6599-1	11.0	EL-1-3	> 320	-	~250	48	-
00121	12.1	121-4	0.3	2	1.4	20	26
00123	12.3	123-5	1.0	4	10	31	35

Some of the detectors described in the above Table were stored for periods of up to 6 weeks at room temperature while exposed to the room atmosphere. In all cases it was possible to operate these devices, when they were cooled back down to -175°C, with no loss in resolution or degradation of reverse bias characteristics. In some cases it was necessary to etch the unprotected n-i-p junction clean of deposits from the air. In other cases even this rudimentary procedure could be omitted.

6. RADIATION DAMAGE MEASUREMENTS

Two germanium-silicon alloy diodes (88 weight percent silicon) and one silicon diode were irradiated with ^{60}Co gamma rays in order to determine the relative amount of radiation damage in the two materials. The alloy devices were prepared from 300 ohm - cm Metallurgie Hoboken p-type material which had been double-doped with boron and gallium. The starting material for the silicon diode was cut from a 1000 ohm - cm Wacker boron-doped crystal. Each of the diodes was fabricated by lithium drifting to a depth of 1 mm. The geometries of the diodes were as follows: silicon - cylinder, 2.2 cm diameter x 2 mm thick; alloy #2 - square, 1 x 1 cm x 2 mm thick; alloy #3 - circular quadrant 1.5 cm^2 surface x 2 mm thick.

After appropriate surface preparation, the diodes were mounted in the vacuum space of a stainless-steel liquid-nitrogen cooled cryostat. Thermal contact between the diodes and the coolant was maintained through a copper surface on which a 1 mm-thick plate of sapphire was fastened. The sapphire served to electrically isolate the diodes from the body of the cryostat (which was common with the ground of the power supply and therefore, functioned as an electrical shield) while providing good thermal contact to the coolant. A 0.010 inch thick sheet of indium was placed on the sapphire to serve as a common contact for the low-voltage side of the diodes. High voltage was applied through three phosphor-bronze spring clips which also served to hold the diodes in place. The clips were each wired to a separate co-axial connector in the wall of the cryostat. A fourth connector was wired to the indium sheet.

Exposure to ^{60}Co gamma rays was accomplished in the hot cell facility of the Rutgers University Reactor. The source consisted of eight adjacent 12-inch pencils containing a total of 3000 curies and held in a horizontal plane

about 0.75 inch below the face of the cryostat, which, in turn, was 0.25 inch below the specimens. This arrangement is depicted in Figure 7. The dose rate at the sample positions was determined by means of thermoluminescent dosimeters which were placed in positions equivalent to those of the diodes for 3 minutes and then read. The gamma ray does rate at the position of the diodes determined in this manner was 217 rads (Si)/sec (±10%). The devices were exposed to a total of 13.7 megarads (Si) (±10%). The variation in dose rate over the detector array was measured to be < 5%.

The samples were cooled to 77°K prior to exposure and maintained at this temperature throughout the irradiation and for two days thereafter. They were then warmed to room temperature in the evacuated cryostat, where they remained for two more days. Each diode was then removed, rinsed in distilled water and methanol, and replaced in the cryostat. Leakage current versus reverse bias voltage was measured, for each of the diodes, immediately before and after exposure using a Keithley 610C electrometer. After the irradiation attempts to determine the counting efficiency and resolution of the diodes for ^{57}Co and ^{133}Ba gamma rays were unsuccessful because a vacuum leak in the cryostat developed during the irradiation. This resulted in a high resistance leakage path between the high voltage connectors and the case of the cryostat but did not effect the leakage-current measurements. The results of these measurements made before and after irradiation are shown for the silicon diode, and the two alloy devices in Figures 8, 9, and 10. The figures also show the reverse leakage current characteristics of the three devices after annealing at room temperature.

Degradation of the reverse current characteristics immediately after exposure is clearly much more severe in the silicon diode (three orders of magnitude at 100V) than in either of the alloy specimens. After annealing at room temperature, the recovery of the silicon diode is not complete. In alloy diode #2 a slight decrease in the leakage current is manifested in the annealed state, compared to the pre-irradiation condition. Diode #3 appears to have undergone a remarkable improvement by the treatment of irradiation plus annealing at room temperature.

7. CONCLUSION

This program has demonstrated that germanium-silicon alloy single crystals of detector grade quality can be produced with as much as 12 weight percent germanium. Operational semiconductor detectors can be made from this material in the p-i-n configuration by the lithium drift technique. As described in Section 3, observed lithium drift rates are considerably slower than would be expected on the basis of the lithium diffusion constant for the alloy as measured between 250°C and 650°C. One possible explanation for the low drift rate is that oxygen is present in the alloy crystal at very low concentration levels. It has been found that the presence of oxygen in sufficient quantities can render a germanium crystal "undriftable". Oxygen atoms act as sites for precipitation of lithium. The longer and deeper the lithium drifts the more deleterious is the effect of the oxygen. The oxygen levels necessary for such adverse behavior need only amount to 1 atom in 10^7. If present in the alloy oxygen should manifest itself through a gross reduction in the lithium mobility at drifting temperatures (130°C). Such an effect is observed since at 130°C the lithium mobility in the alloy is found to be many orders of magnitude

lower than anticipated. When the value of the mobility of lithium in the alloy was measured at temperatures between 250°C and 650°C it was found to be very close to the mobility value for lithium in silicon. This apparent anomaly is due to the fact that at the elevated temperatures the presence of oxygen in the alloy does not have a pronounced effect on the lithium mobility. Additional evidence pointing to oxygen as the possible source of difficulty lies in the fact that the one alloy ingot from which no detectors could be made (00122) had the highest resistivity and therefore the lowest dopant concentration. The presence of small quantities of oxygen can be negated by increasing the doping level. Thus the lower resistivity crystals with a higher gallium and boron level did not manifest the complete lack of suitability for detector fabrication shown by the high resistivity crystal. The upper limit to the dopant level is determined by the number of dopant atoms that one is willing to accept in the semiconductor material. Each dopant atom must be compensated by a lithium atom in order to make a good lithium drifted detector. The addition of too many of these impurity sites to the crystal will degrade the detector characteristics. The carrier lifetime measurements described in Section 3 support the above argument by indicating the presence of a considerable number of impurity sites in the unlithiated alloy samples.

Detectors fabricated from the germanium-silicon alloy show charged particle resolution comparable to that obtained with silicon detectors. The alloy detector can be operated at temperatures close to room temperature with good resolution. By modifying the detector geometry room temperature operation should be feasible. Prolonged storage of these devices at 20°C does not appear to affect them adversely. On the other hand, it is known that lithium will precipitate from compensated germanium stored at this temperature.

Germanium-silicon single crystal alloy detectors should prove useful for charged particle detection in earth satellites. A thermoelectric cooler could be employed in such an application to obtain operating temperatures of -75°C. Based on the results of the preliminary radiation damage studies the germanium-silicon alloy appears to evidence a high degree of insensitivity to radiation damage when compared to ^{60}Co induced damage in a silicon detector. Almost complete recovery of radiation induced damage can be achieved with the alloy detector by use of an appropriately chosen annealing cycle. The insensitivity of the alloy to radiation damage from ^{60}Co gamma rays, even before annealing, may be due to recombination which can take place spontaneously in the alloy at -195°C. Further experimental investigation in this area is in progress.

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5. See for example -
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APPENDIX A

In an effort to locate germanium-silicon alloy, the suppliers of silicon and germanium listed below were contacted. Attempts were also made to contact researchers who had published papers involving silicon-germanium single crystal work in case they might be able to provide Ge-Si crystals for this program. Listed below is a summary of these contacts.

	Source	Response
1.	Semi-Metals, Inc.	Alloy not available.
2.	Metallurgie Hoboken (Belgium)	Produced alloy (see Appendix B)
3.	Materials Research Corp.	Had never made alloy but was willing to try. Isotopes judged this company unsuitable at the present time.
4.	Wacker Chemical Company (Germany)	Not interested.
5.	Elmat Corp.	Ingots delivered (see Appendix B)
6.	Monostructures International	Obtained ingot (see Appendix B)
7.	Sylvania Electric Inc.	No single crystal alloy.
8.	Monsanto Chemical Corp.	No single crystal alloy.
9.	Dow Corning Corp.	No single crystal alloy.
10.	Semi-Elements Inc.	Isotopes ordered one ingot but it had a negligible germanium content.
11.	General Diode Corp.	Ingots delivered (see Appendix B)
12.	Vieille-Montagen (France)	No single crystal alloy.
13.	R.C.A. Research Group	Kindly supplied Isotopes with a Ge-Si alloy ingot which was made some years ago. This ingot (7% germanium by weight) was not sufficiently pure for detector fabrication. R.C.A. did not wish to make high purity alloy ingots at this time (see Appendix B).
14.	Geoscience Instruments Corp.	An order was placed but afterward company decided that it did not wish to fabricate the alloy.

	Source	Response
15.	Ventron Electronics Corp.	Several crystals were ordered. One was delivered but it had a very low germanium content (see Appendix B)
16.	General Electric Research Laboratory	Not interested in making Ge-Si alloy.
17.	Bell Telephone Laboratories	Not interested in making alloy.
18.	G.E.C. Research Laboratories (England)	No single crystal Ge-Si alloy.
19.	Royal Radar Establishment (England)	Interested in making the alloy but no work done in that area at present.
20.	University of California at Los Angeles, Brown University, Oxford University (England)	Contracted various individuals who had worked in field but obtained no alloy as a result of discussions.

APPENDIX B

Germanium-silicon alloy crystals were received from six manufacturers: General Diode Corp., R.C.A. Research Laboratories, Ventron Electronics Corp., Monostructures International, Elmat Corp., and Metallurgie Hoboken. An evaluation of these crystals is presented below:

Manufacturer	Ingot No.	Resistivity	Weight % Germanium	Comments
General Diode Corp	22	10-25Ω cm	3.14	It was concluded that General Diode Corp was unable to produce alloy with the high germanium concentrations required.
	28	320-390	< 3	
	32	66-210	< 3	
	39	66-69	0.81	
	45	120-150	2.77	
	52	10-15	< 3	
	83	150-300	< 3	
	84	500-1200	< 3	
	85	50-225	1.57	
R.C.A. Labs	-	3-6	7	Too many impurities were present to make good detectors.
Ventron Electronics	-	-	8.3	Polycrystaline
Monostructures	-	10-20	1.08	Too many impurities were present to make good detectors.
Elmat Corp	6599-1	~200	11.0	This crystal produced acceptable detectors.
	6599-2	~200	11.0	Crystal showed twinning.
Matallurgie Hoboken	00121	23-30	12.1	Acceptable detectors were produced from these crystals.
	00122	200-400	10.5	
	00123	155-245	12.3	

FIGURE CAPTIONS

Figure 1. Resistance versus depth profile in lithium diffused germanium-silicon alloy containing 10% germanium by weight. The diffusion profile is determined by four point probe measurements taken after successive lapping of the n face. This diffusion took place for 10 minutes at 550°C in p-type alloy whose resistivity was 307 ohm-cm.

Figure 2. Lithium drift depth in germanium-silicon alloy containing 10% germanium by weight, as a function of time at various temperatures. Also shown for comparison are drift curves in germanium and in silicon.

Figure 3. Assembly for lithium drift compensation of the germanium-silicon alloy.

Figure 4. Schematic of electronic system for gamma ray spectroscopy.

Figure 5. Reverse bias current characteristic taken at three different temperatures. The measurements were performed on germanium-silicon alloy charged particle detector 00121-4.

Figure 6. ^{241}Am alpha spectrum as observed with germanium-silicon alloy detector 00121-4 operated at -196°C. The high energy portion of the ^{133}Ba gamma ray spectrum recorded at the same time is shown on the truncated channel scale at the left. The energies associated with the various gamma and alpha lines are also indicated.

Figure 7. Geometry of radiation damage study. Eight ^{60}Co pencils contained 3000 curies. The diodes were mounted on the bottom of the copper disc. The plane of the disc is 1 inch above the plane of the axis of the pencils. The center to center separation of each pencil was 5/8 inches and the pencil diameter was 1/2 inch.

Figure 8. Reverse leakage current versus bias for a lithium-drifted silicon diode at 77°K before irradiation (X), immediately after exposure to 2.3×10^{16} ^{60}Co gamma rays per cm^2 (●), and after a two-day room-temperature anneal following exposure (▲).

Figure 9. Reverse leakage current versus bias for alloy diode #2 at 77°K before irradiation (X), immediately after exposure to 2.3×10^{16} ^{60}Co gamma rays per cm^2 (●), and after a two-day room-temperature anneal following exposure (▲).

Figure 10. Reverse leakage current versus bias for alloy diode #3 at 77°K before irradiation (X), immediately after exposure to 2.3×10^{16} ^{60}Co gamma rays per cm^2 (●) after a two-day room-temperature anneal following exposure (▲).

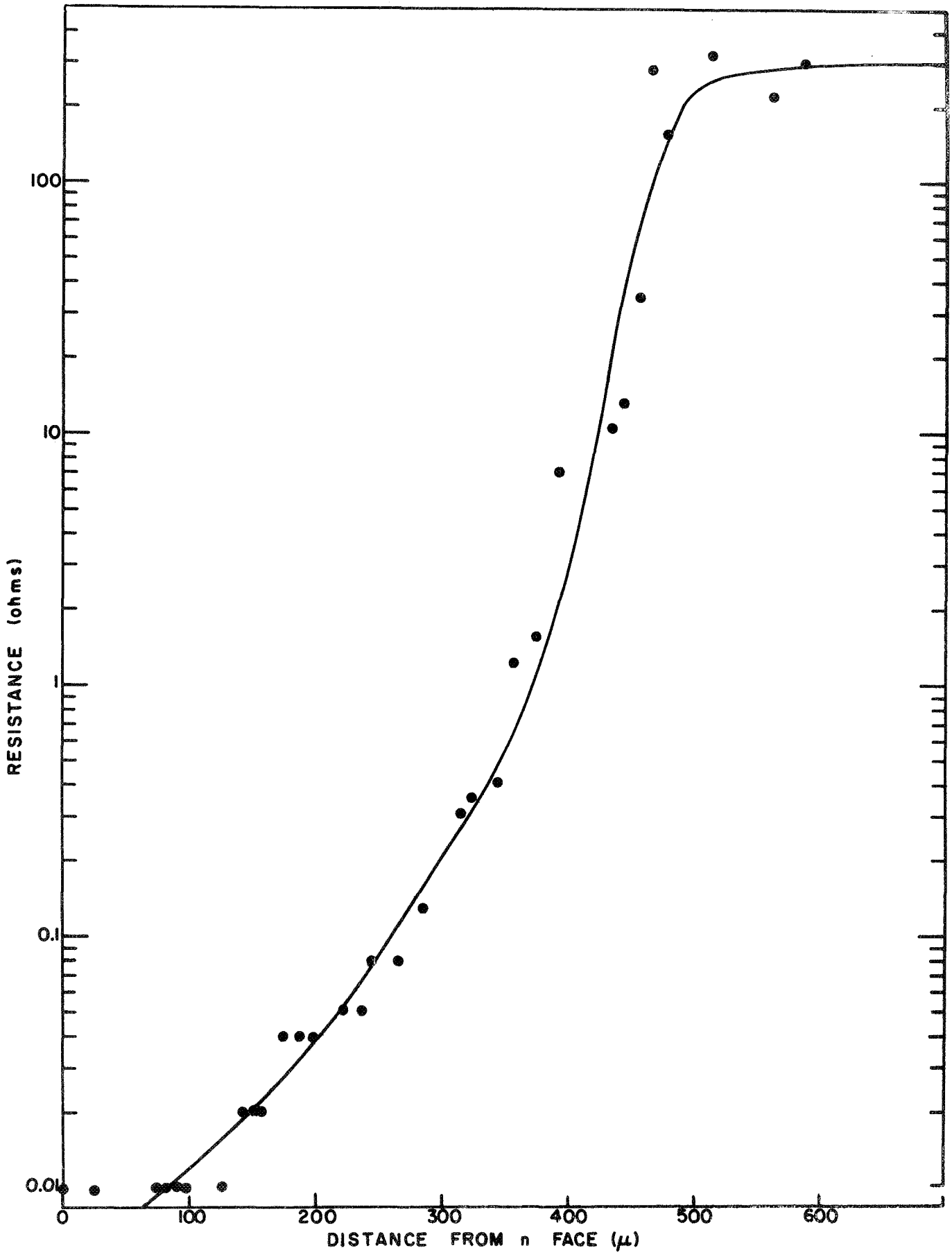
RESISTANCE (ohms)
100
10
1
0.1
0.01
0
100
200
300
400
500
600
DISTANCE FROM n FACE (μ)

FIGURE 1

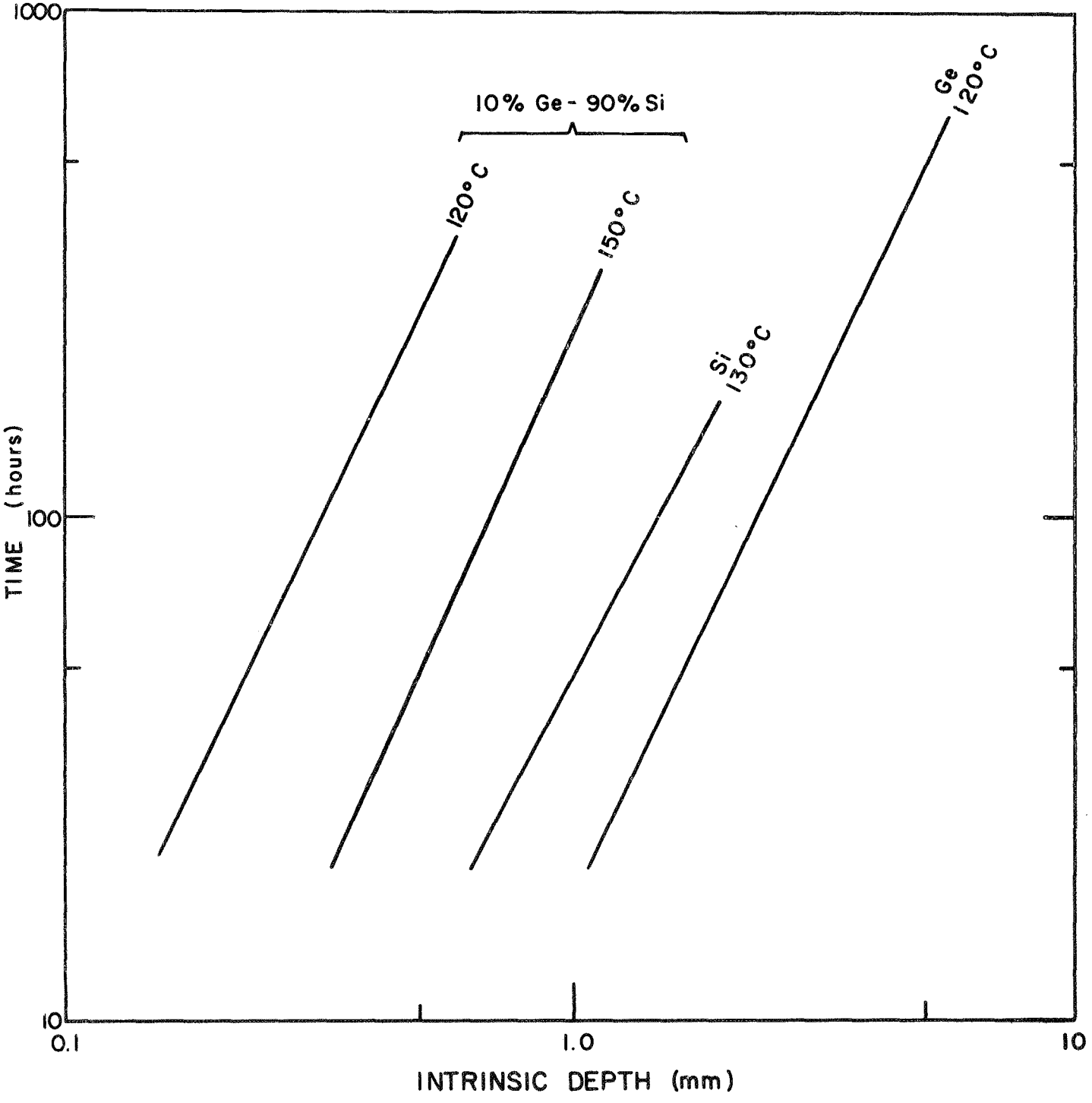
1000
100
10
TIME (hours)
10% Ge - 90% Si
120°C
150°C
Si
130°C
Ge
120°C
0.1
1.0
10
INTRINSIC DEPTH (mm)

FIGURE 2

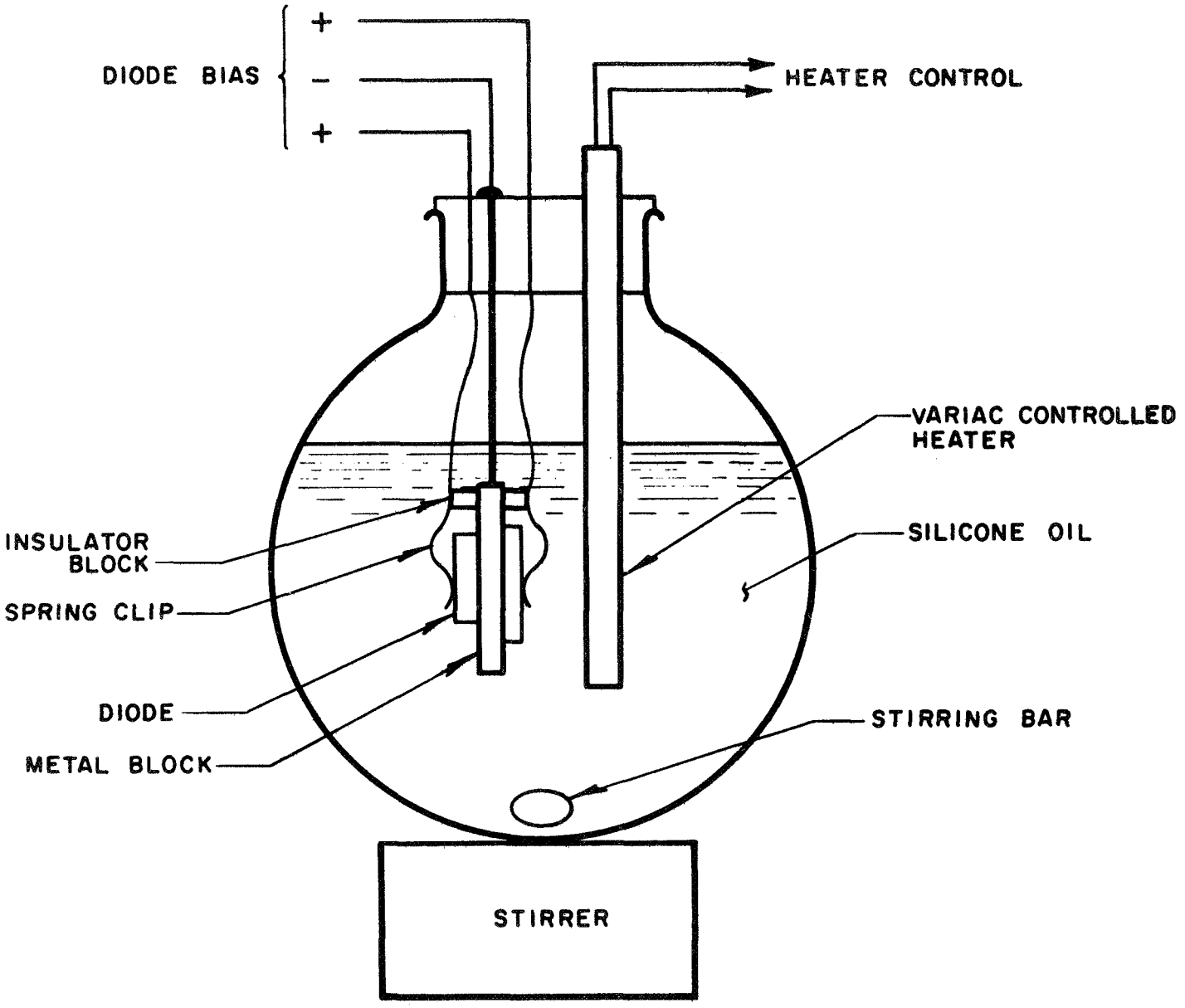
DIODE BIAS
+
−
+
HEATER CONTROL
VARIAC CONTROLLED HEATER
SILICONE OIL
INSULATOR BLOCK
SPRING CLIP
DIODE
METAL BLOCK
STIRRING BAR
STIRRER

FIGURE 3

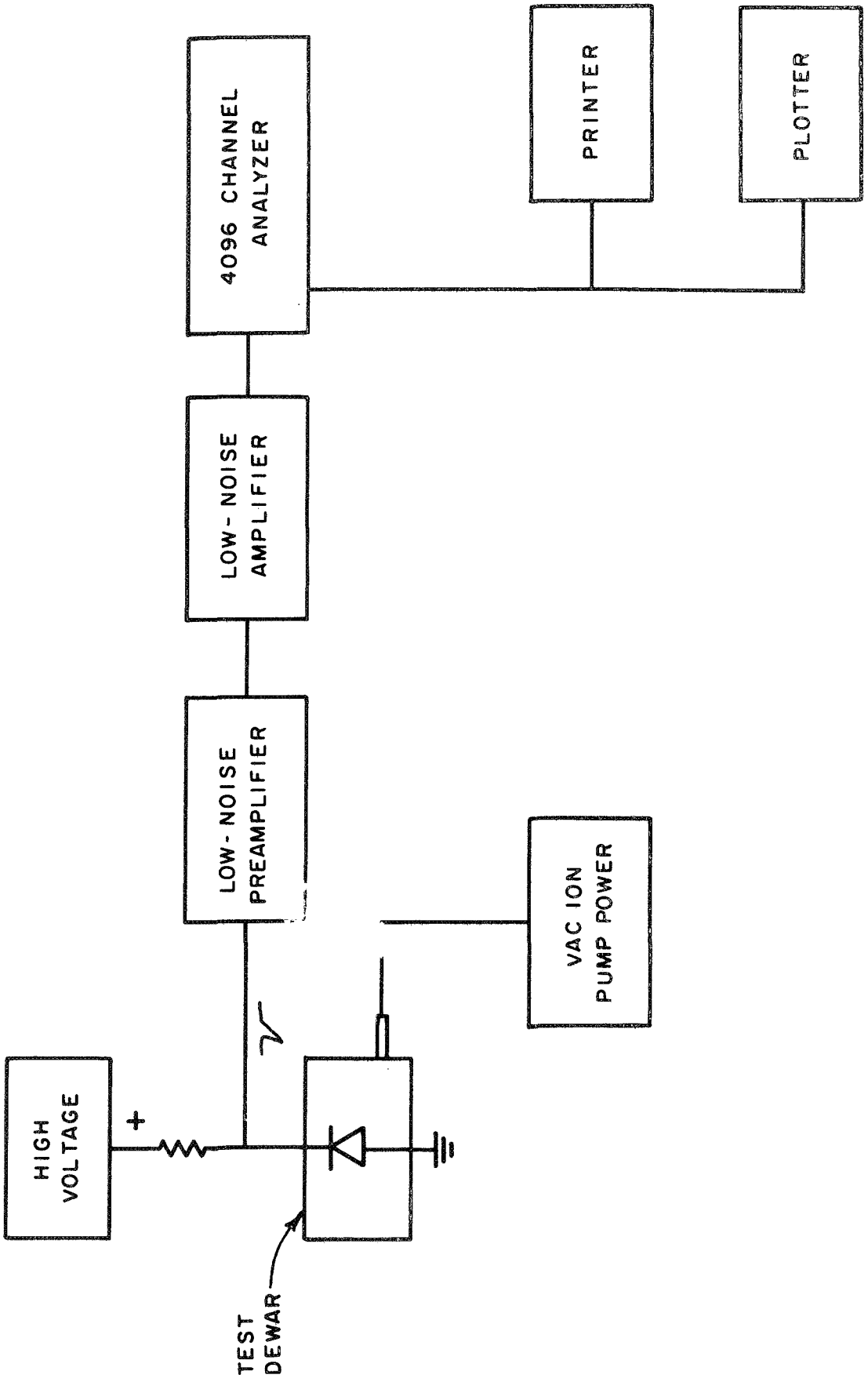
4096 CHANNEL ANALYZER
PRINTER
PLOTTER
LOW-NOISE AMPLIFIER
LOW-NOISE PREAMPLIFIER
VAC ION PUMP POWER
HIGH VOLTAGE
+
TEST DEWAR

FIGURE 4

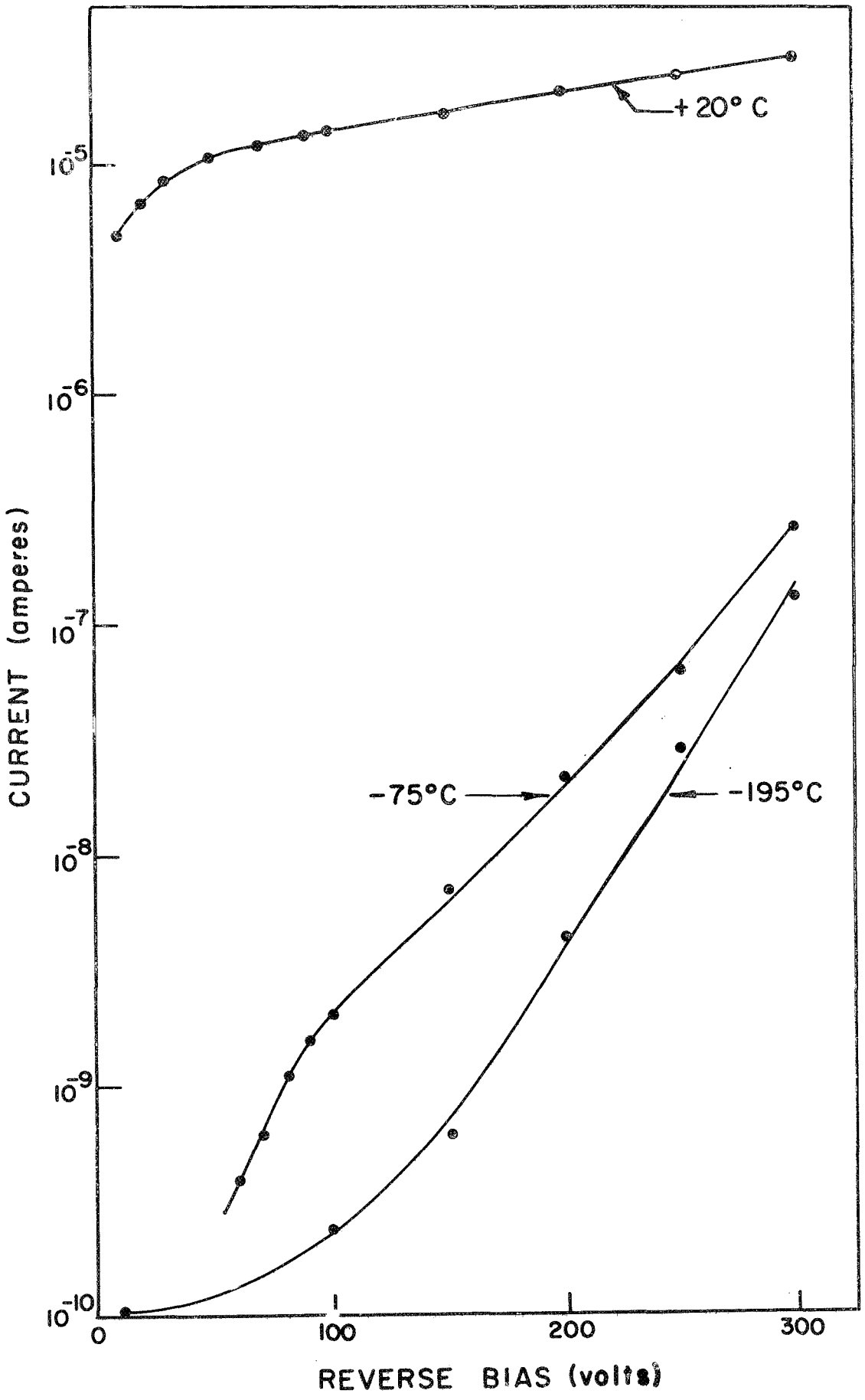
+20° C
-75°C
-195°C
CURRENT (amperes)
REVERSE BIAS (volts)
10-5
10-6
10-7
10-8
10-9
10-10
0
100
200
300

FIGURE 5

CHANNEL NUMBER
80
100
1360
1380
1400
1420
0
2
4
6
8
10
COUNTS (arbitrary units)
133Ba - Gamma Rays
303.1 keV
356.3 keV
384.1 keV
241Am - Alphas
5.477 MeV
5.435 MeV
5.500 MeV
5.534 MeV
20 keV

FIGURE 6

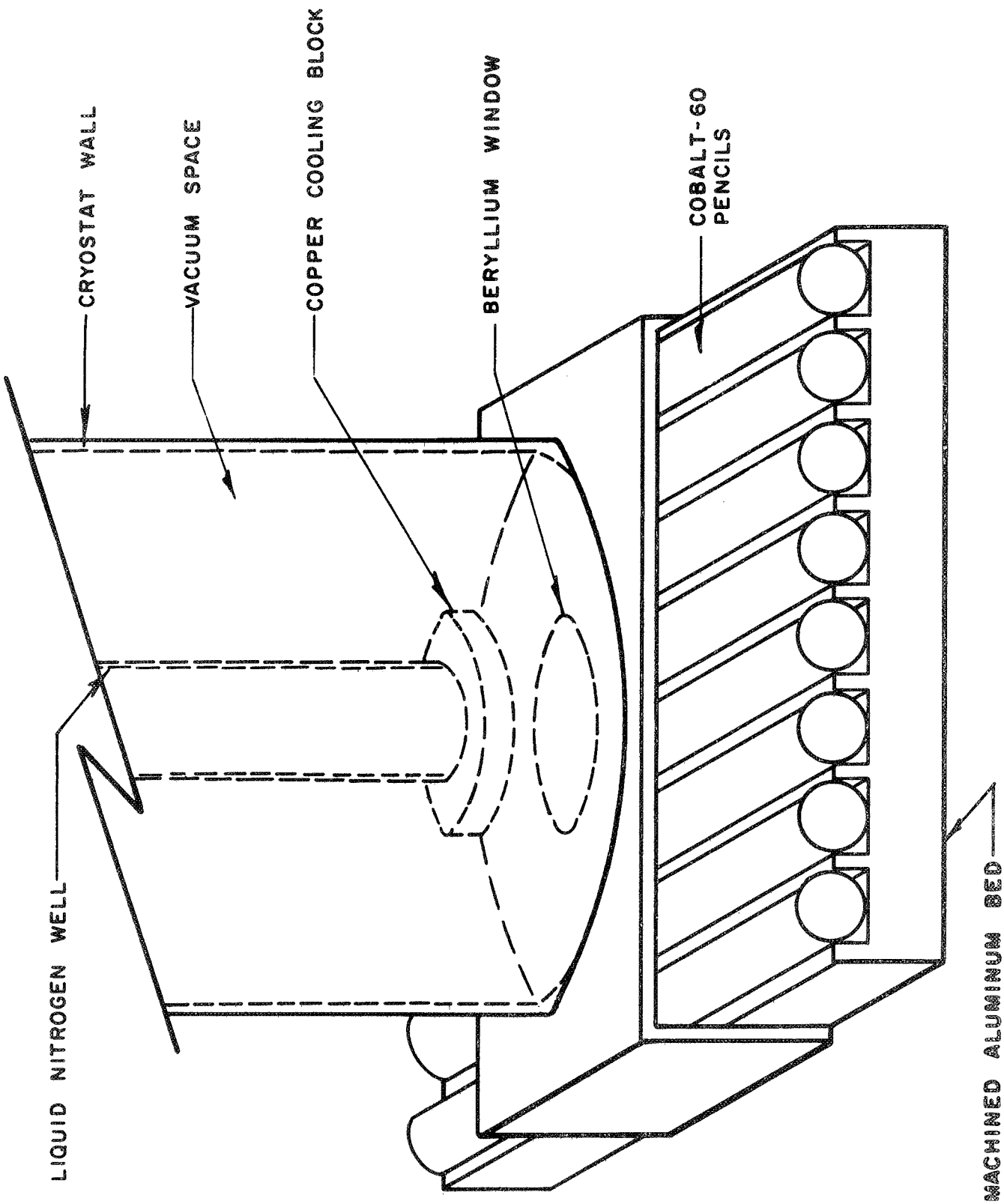
CRYOSTAT WALL
VACUUM SPACE
COPPER COOLING BLOCK
BERYLLIUM WINDOW
COBALT-60 PENCILS
LIQUID NITROGEN WELL
MACHINED ALUMINUM BED

FIGURE 7

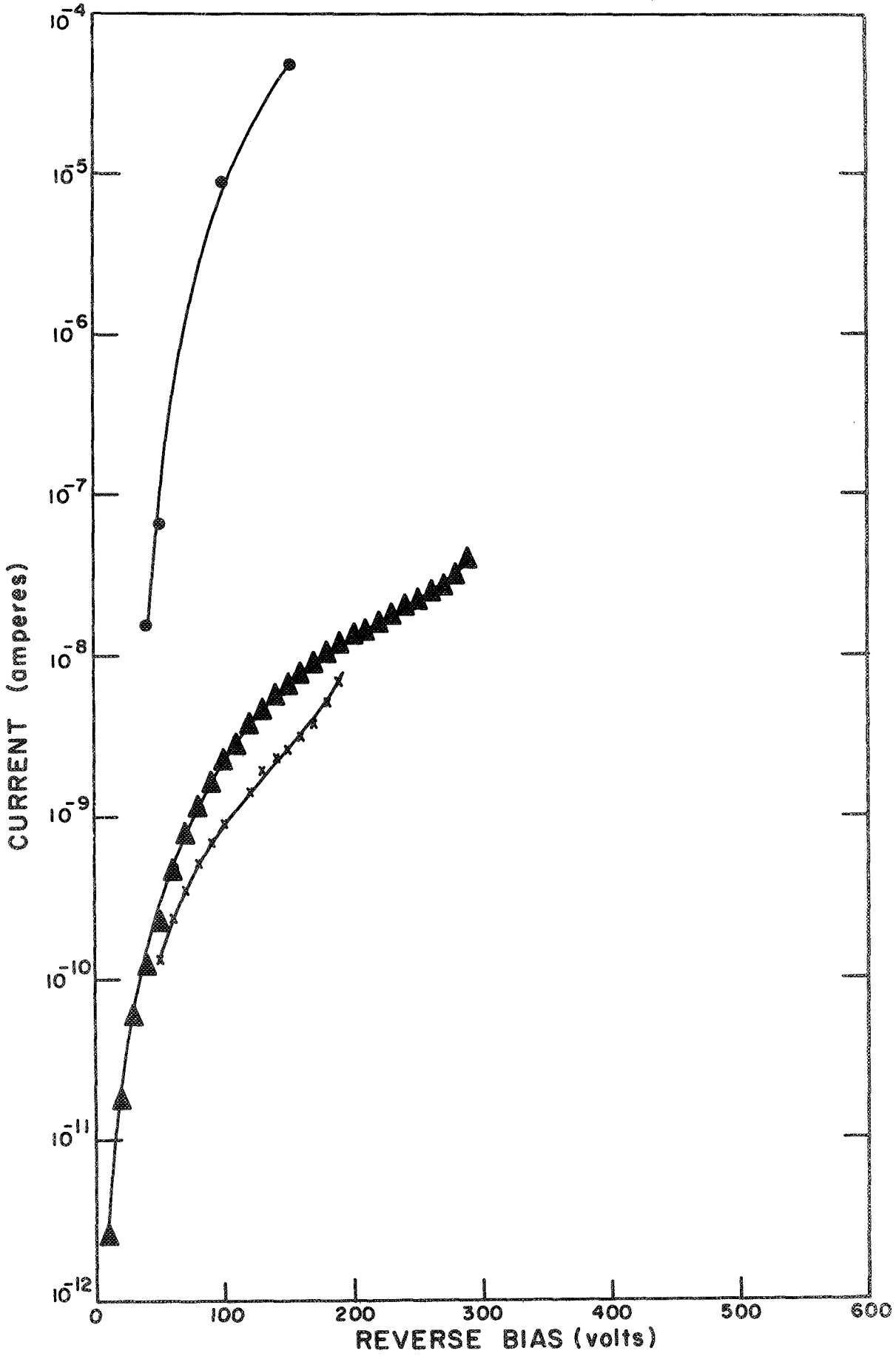
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
CURRENT (amperes)
0
100
200
300
400
500
600
REVERSE BIAS (volts)

FIGURE 8

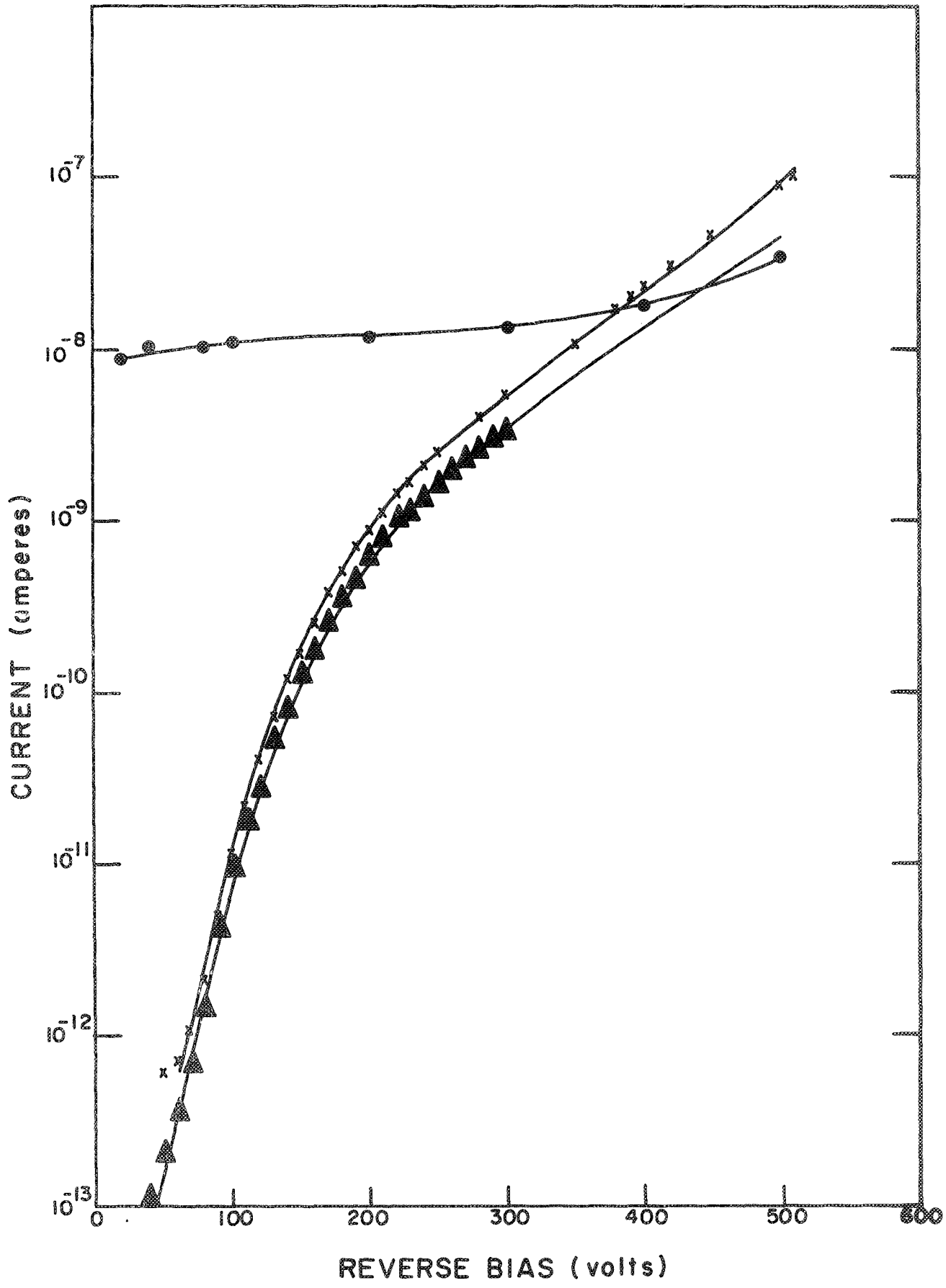
CURRENT (amperes)
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
0
100
200
300
400
500
600
REVERSE BIAS (volts)

FIGURE 9

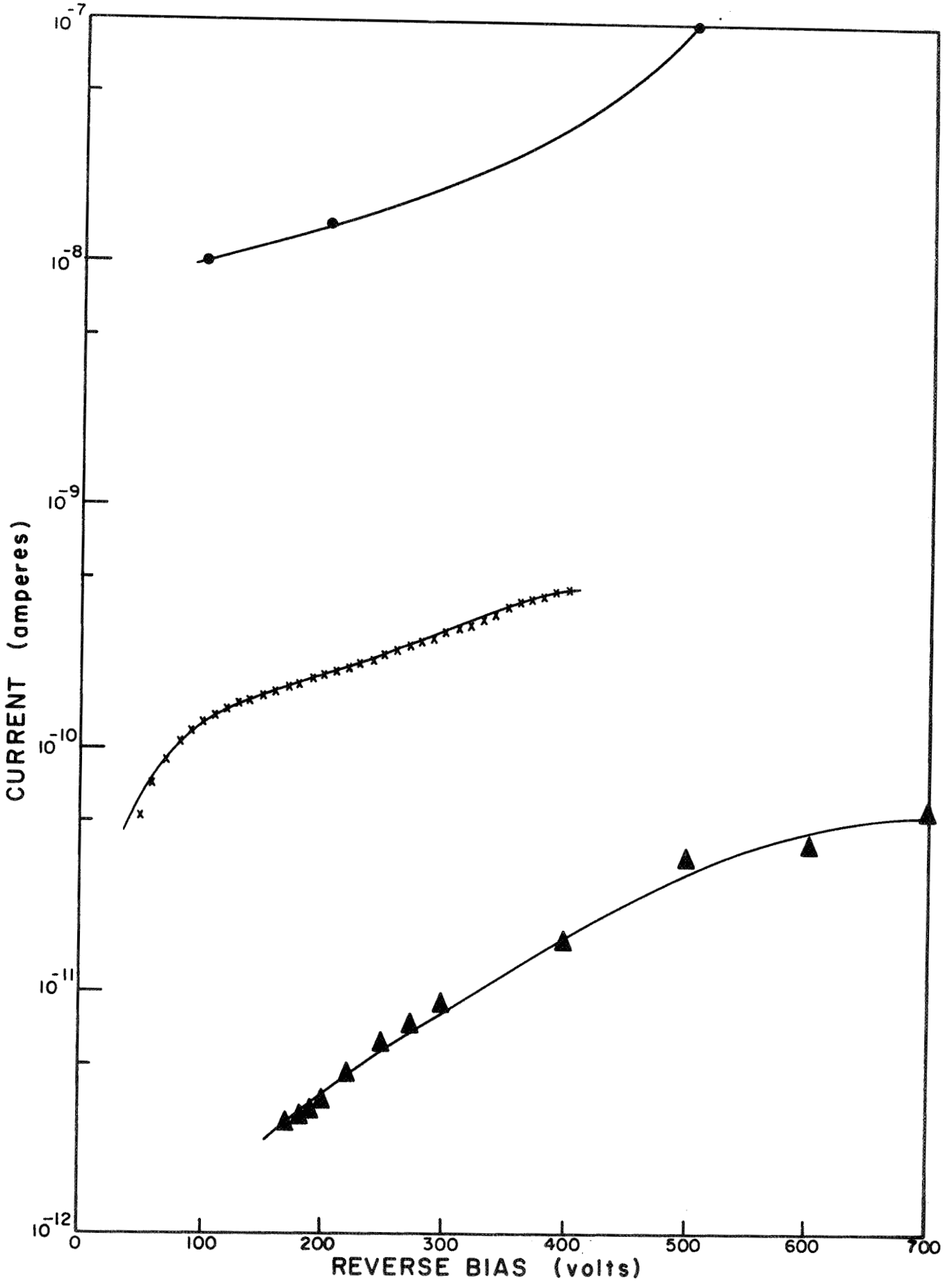
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
CURRENT (amperes)
0
100
200
300
400
500
600
700
REVERSE BIAS (volts)

FIGURE 10